



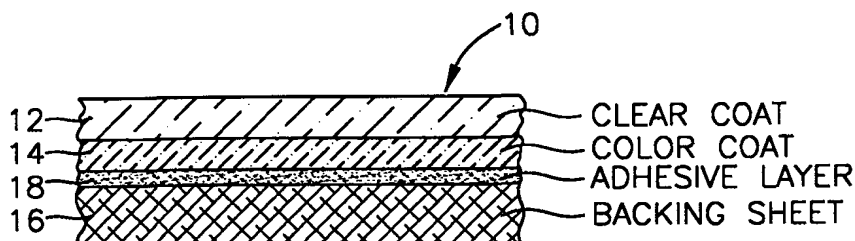
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B32B 31/30, 27/20, 27/30, B29C 51/14 //</b> <b>B29K 27:12, 33:04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/64241</b> <b>(43) International Publication Date:</b> 16 December 1999 (16.12.99)
<b>(21) International Application Number:</b> PCT/US99/12668 <b>(22) International Filing Date:</b> 7 June 1999 (07.06.99)  <b>(30) Priority Data:</b> 09/093,471                      8 June 1998 (08.06.98)                      US  <b>(71) Applicant (for all designated States except US):</b> AVERY DENNISON CORPORATION [US/US]; 150 North Orange Grove Boulevard, Pasadena, CA 91103 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ROYS, John, E. [US/US]; 286 Island Drive, Lowell, IN 43656 (US). ENLOW, Howard, H. [US/US]; 1334 Camellia, Munster, IN 46431 (US). MARTUS, Paul, J. [US/US]; 5051 Summer Road, North Branch, MI 48461 (US).  <b>(74) Agent:</b> MAXWELL, Walter, G.; Christie, Parker & Hale, LLP, P.O. Box 7068, Pasadena, CA 91109-7068 (US).		<b>(81) Designated States:</b> BR, CA, CN, JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** THICK SHEET LAMINATION PROCESS FOR MAKING EXTERIOR AUTOMOTIVE BODY PANELS

**(57) Abstract**

An exterior automotive quality paint coat is laminated to the surface of a plastic car body member of panel. A dry paint transfer film is first laminated to a relatively thin semi-rigid thermoformable resinous backing sheet. The backing sheet side of the resulting laminate is then laminated to a



relatively thick thermoformable substrate sheet comprising the same or a compatible polymeric material. The two sheets are joined by extruding the thick substrate sheet and using the heat of extrusion to then laminate the thin backing sheet to the thicker extruded substrate sheet. The resulting thick sheet laminate is then thermoformed, preferably by first heating the laminate to a forming temperature, followed by vacuum forming the laminate to a three-dimensional shape of the finished automotive part, such as a fascia, ready to put on a vehicle.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

1                   THICK SHEET LAMINATION PROCESS FOR MAKING  
                    EXTERIOR AUTOMOTIVE BODY PANELS

5                   FIELD OF THE INVENTION

                    This invention relates to the manufacture of exterior automotive body panels or members made from polymeric materials, and more particularly, to a dry paint transfer-lamination process for applying preformed paint film laminates to plastic substrate sheet materials. The process avoids the separate step of injection molding a substrate panel to the dry paint transfer laminate.

10                  BACKGROUND OF THE INVENTION

                    Exterior automotive body panels have been made in the past by spray painting sheet metal parts. Multi-layer paint coats, such as those referred to as clear coat/color coat paint systems, have been used to produce desirable optical effects. In addition to high gloss and high distinctness-of-image (DOI), these paint coats also are highly durable by providing chemical  
15                  resistance, abrasion resistance and weatherability that avoids degradation by ultraviolet light.

                    In more recent years, molded plastic car body panels have been made with decorative clear coat/color coat paint films bonded to the molded plastic panel. Use of such films avoids certain environmental problems associated with evaporation of paint solvents while also reducing or eliminating the need for paint facilities and emission controls at the automotive production  
20                  plant.

                    Because of the growing need to reduce atmospheric pollution caused by solvents emitted during the painting process, many different approaches have been taken in recent years for producing these decorative films. These processes can be generally categorized by solution-casting techniques or extrusion techniques. For instance, U.S. Patent No. 5,707,697 to Spain  
25                  et al. describes solution-casting techniques in which liquid-cast solvent-based clear coats and pigmented base coats are applied to a flexible casting sheet by a coating process such as reverse roll coating. The liquid-cast layers are separately applied and then dried at high temperatures to evaporate the solvents. Following the steps of casting the clear coat and color coat, the composite paint coat is removed from the carrier and transfer laminated to a thin, semi-rigid,  
30                  thermoformable polymeric backing sheet. The preferred backing sheet is about 20 mils in thickness, although the backing sheet can have a thickness from about 10 mils to about 40 mils. The paint coated backing sheet is then thermoformed into a desired three-dimensional shape, followed by molding the substrate panel to the thermoformed sheet in an injection mold. This process, known as the "insert-mold" process, together with the transfer-lamination and  
35                  thermoforming steps, are described in the above-mentioned '697 patent which is incorporated herein by this reference.

                    As an alternative to solvent-cast films, extruded films have been used for making exterior automotive clear coat/color coat paint films. International Application WO 96/40480 to Enlow

1 et al., which is incorporated herein by this reference, describes an approach in which paint films  
and/or laminates are made by extrusion coating or coextrusion techniques. The paint film is  
transferred to a supportive backing sheet by transfer-lamination techniques, followed by  
thermoforming the paint coated backing sheet into a desired three-dimensional shape and  
5 injection cladding it to a substrate panel by the insert-mold process.

As a further alternative, a dry paint transfer sheet can be placed directly in an injection  
mold without thermoforming it outside the mold. The sheet in this instance is formed into a  
contoured shape under heat and pressure in the injection mold by the molding material in what  
is referred to as the "in-mold" process. Such a process, for example, is described in U.S. Patent  
10 No. 4,810,540 to Ellison et al.

The present invention is based on a recognition that production costs for making these  
exterior automotive parts can be reduced by eliminating the injection-molding step. In other  
words, it can be desirable to manufacture an exterior automotive body member or panel so that  
the finished automotive part, such as a facia, is ready to put on the vehicle after the  
15 thermoforming step. This would require producing a polymeric substrate sheet with sufficient  
thickness and structural integrity to function as the finished part that adequately supports the  
transferred paint film. This also requires a polymeric substrate material that can be shaped by  
thermoforming techniques while not interfering with the desired optical properties (such as high  
distinctness-of-image and gloss) of the finished paint film. For instance, may be desirable to use  
20 polymeric substrate materials that contain high filler or regrind components in order to reduce  
the cost of the overall product. But these particulate materials can be transmitted from the  
substrate to the paint film during thermoforming, creating imperfections that degrade the  
otherwise desired smooth, high quality optical surface of the finished film. In addition, the  
thicker substrate sheet material can absorb substantial amounts of heat when bonding a paint film  
25 to it or when thermoforming it. Such excessive heat absorption can be transferred to the paint  
film surface and degrade the optical properties of the paint film by causing excessive haze or  
fogging of the clear coat. This problem is particularly critical when such exterior paint films are  
made from fluoropolymer resins, such as polyvinylidene fluoride (PVDF) and acrylic resin alloys  
of the types described in the above-mentioned '697 patent to Spain et al., International  
30 Application WO 96-40480 to Enlow et al., or the '540 patent to Ellison et al.

#### SUMMARY OF THE INVENTION

Briefly, one embodiment of this invention provides a process for making exterior  
automotive quality body members or panels from a preformed dry paint transfer laminate  
35 comprising an exterior automotive quality paint film applied to a relatively thin, semi-rigid,  
thermoformable polymeric backing sheet. The process includes the step of extruding a relatively  
thick sheet of a thermoformable polymeric material and forming a paint coated thick sheet  
laminate by laminating the backing sheet side of the preformed dry paint laminate to the extruded

1 sheet. The lamination step is carried out using the heat of extrusion to heat bond the backing  
sheet and extruded sheet together to form an integral substrate sheet which is thermoformable  
to a three-dimensional shape with the dry paint film bonded to its exterior surface. The backing  
sheet and extruded sheet comprise compatible polymeric materials to promote the bond between  
5 them. In one embodiment the extruded sheet has a thickness of at least twice the thickness of  
the backing sheet. In another embodiment the backing sheet has a thickness from about 10 mils  
to about 30 mils, and the extruded substrate sheet has a thickness of at least about 40 mils. In  
forming the thick sheet laminate to a desired shape, heat is initially applied to the laminate to  
gradually raise the substrate temperature to the forming temperature. This step is followed by  
10 forming the laminate to a three-dimensional shape, preferably by vacuum forming, to produce  
a finished exterior automotive quality body panel or member.

The present invention provides a process for manufacturing a high quality exterior  
automotive paint finish (high gloss and high DOI) on a body member of panel of a thickness up  
to about 0.250 inch, by first laminating the dry paint transfer film to the relatively thin polymeric  
15 backing sheet, and subsequently laminating the backing sheet to the substantially thicker  
extruded substrate sheet. The intermediate backing sheet provides a barrier that prevents  
transmission of defects from filler and regrind materials contained in the substrate sheet material  
to the paint film surface, thereby preserving the high quality optical properties of the finished  
film during thermoforming to a finished three-dimensional shape.

20 A primary advantage of the process is the elimination of a subsequent injection molding  
step. This greatly reduces production costs because the high cost of an injection molding tool  
is avoided. Processing time also is reduced.

As mentioned, the paint film-backing sheet laminate is heat-bonded to the extruded  
substrate sheet, using the heat of extrusion to bond the backing sheet to the extruded substrate.  
25 This lowers production costs by reducing the overall number of steps in the process, when  
compared with laminating the backing sheet to a preformed substrate sheet or molded sheet.

In one form of the invention, the extruded substrate sheet is rapidly cooled following  
extrusion and prior to lamination to the dry paint transfer laminate. This avoids high levels of  
heat being transmitted to the paint film which could otherwise be at a level sufficient to cause  
30 haze or other degradation of the optical properties of the paint film. Haze is undesirable not only  
in the clear coat (because it lowers gloss and DOI) but also in the color coat, because it can  
produce undesired color changes causing difficulties in color matching. Further, preferred  
thermoforming techniques include preheating the extruded substrate sheet under controlled  
heating conditions prior to thermoforming. This can reduce the amount of heat to which the  
35 paint film is exposed during thermoforming to further control excessive heat transmission to the  
paint film.

These and other aspects of the invention will be more fully understood by referring to the  
following detailed description and the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view illustrating one embodiment of a preformed laminate comprising an exterior automotive quality dry paint transfer film adhered to a thin, semi-rigid polymeric backing sheet.

FIG. 2 is a schematic side elevational view showing a coextrusion process for making the backing sheet and adhesive layer component of the laminate shown in FIG. 1.

FIG. 3 is a schematic side elevational view showing a process for transfer-laminating a dry paint transfer film to a backing sheet.

FIG. 4 is a schematic side elevational view showing a process for extrusion lamination to make thick sheets.

FIG. 5 is an alternative embodiment of the extrusion lamination process of FIG. 4.

FIG. 6 is a schematic view illustrating thermoforming of the thick sheet laminate produced by the steps shown in FIG. 4.

FIG. 7 is a schematic cross-sectional view showing the finished part following thermoforming to a three-dimensional contour.

FIG. 8 is a schematic side elevational view showing a process for twin sheet forming a reinforced finished part.

## DETAILED DESCRIPTION

An exterior automotive quality paint film is applied to a polymeric substrate sheet by a combination of steps which include forming a dry paint transfer film of exterior automotive quality, transferring the dry paint film to a thin supporting backing sheet, laminating the resulting preformed dry paint film laminate to an extruded thick substrate sheet, and thermoforming the resulting paint coated laminate to the shape of a finished part. FIG. 1 illustrates one embodiment of the invention in which the initial dry paint transfer laminate 10 comprises an exterior automotive base coat/clear coat paint film which includes an outer clear coat 12 and an underlying pigmented color coat 14. The clear coat/color coat paint film can comprise any exterior automotive dry paint transfer film which is weatherable, durable, thermoformable, and has thermoplastic properties in the sense that the paint film can be subjected to elongation under application of heat in a thermoforming process to shape the film to a finished three-dimensional contour while retaining exterior automotive durability and optical properties required for exterior automotive use. In one preferred form of the invention, the clear coat layer is preferably a dry paint film having a thickness of about 0.5 to about 1.5 mils. For metallic paint films, the clear coat can have a thickness up to about 2 mils. The clear coat preferably comprises a blend of a thermoplastic fluorinated polymer and an acrylic resin. The preferred clear coat preferably contains a thermoplastic fluorocarbon such as polyvinylidene fluoride (PVDF). The fluorinated polymer can comprise a homopolymer or copolymers and terpolymers of vinylidene fluoride. The acrylic resin component of the clear coat can be a polymethyl methacrylate or a polyethyl

1 methacrylate resin or mixtures thereof. A preferred formulation comprises from about 50% to  
about 70% PVDF and from about 30% to about 50% acrylic resin, based on the total resin solids  
in the paint film. Formulations suitable for preparing clear coat paint films useful in practicing  
this invention are described in more detail in U.S. Patent 5,707,697 to Spain et al. which is  
5 incorporated herein by reference.

The Spain, et al. '697 patent discloses solvent-casting techniques that can be used for  
making the base coat/clear coat paint film. According to that process, the clear coat and color  
coat are cast in sequence on a polyester carrier sheet and dried to evaporate the solvents. The  
clear coat is cast on a high gloss, smooth polyester casting film in order to transfer high quality  
10 optical properties to the clear coat surface.

The color coat 14 is cast on the clear coat after the clear coat has been dried on the carrier  
sheet. The color coat can be coated on the dried clear coat, or the color coat can be coated on  
a separate polyester casting film, dried, and later transferred from the casting film to the clear  
coat. In either case, the color coat is preferably applied to the casting film by reverse roll  
15 coating, comma coating, or die coating techniques similar to those used in forming the solvent-  
cast clear film. The color coat preferably comprises a thermoplastic synthetic resinous coating  
composition containing a level of pigment and/or metallic flakes to provide the necessary  
appearance for exterior automotive use of the finished part. The color coat contains a sufficient  
amount of pigment to maintain sufficient opacity and distinctness-of-image while avoiding stress  
20 whitening throughout the thermoforming step so as to function as an exterior automotive paint  
coat. The pigmented base coat may contain a sufficient amount of reflective flakes to provide  
metallic base coat/clear coat paint films and their resulting desirable optical properties, if desired.  
The preferred dry film thickness of the color coat is about 0.5 to about 1.5 mils. In a preferred  
form of the invention, the color coat comprises a blended thermoplastic fluorinated polymer and  
25 acrylic resin paint system similar to the paint system used in forming the clear coat. As with the  
clear coat, suitable color coat formulations also are described in the previously referenced Spain  
et al. '697 patent.

As an alternative to the base coat/clear coat paint film of FIG. 1, the exterior automotive  
paint film may include a combination exterior clear coat and a tint coat, or the paint coat may  
30 comprise a single dry thin film coating of a pigmented synthetic resinous material having desired  
exterior automotive properties. Alternatively, the base coat/clear coat paint film may be  
produced by extrusion coating techniques such as those described in International Application  
WO 96/40480 to Enlow et al. which is incorporated herein by reference.

Whether the paint film is made from solvent casting techniques or extrusion coating  
35 techniques, in either instance the dry paint transfer film is laminated to a thermoformable  
backing sheet 16 with an intervening adhesive layer or size coat 18. The backing sheet is a semi-  
rigid, self-supporting, thin, flat sheet of a thermoformable polymeric material. The backing sheet  
is made from a material having a thickness capable of thermoforming into a complex three-

1 dimensional shape while protecting the outer paint film from transmission of defects from an  
underlying substrate sheet 56 described below. The material from which the substrate sheet is  
made can contain a substantial amount of filler or regrind particles and therefore can produce  
imperfections in the surface of the finished article. The backing sheet has a thickness in the  
5 range from about 10 mils to about 30 mils. The preferred material from which the backing sheet  
is made is ABS, thermoplastic olefins (TPO), or other olefinic materials containing  
polypropylene or polyethylene. The thickness of the backing sheet is sufficient to absorb defects  
from the underlying substrate sheet to avoid transmission of defects to the surface of the paint  
film. The backing sheet material also is of substantially higher grade than the underlying  
10 substrate material. The higher quality backing sheet material has a substantially lower gel count  
than the substrate material. The substrate material also can contain filler and a regrind content  
up to about 30% of its total volume and/or weight. Such filler and regrind materials are  
essentially absent from the backing sheet material.

FIG. 2 illustrates one process for making a composite backing sheet and adhesive layer  
15 by coextrusion techniques. Alternatively, a single-layer preformed backing sheet can be adhered  
to an adhesive size coat which has been coated on the color coat side of the dry paint film. The  
size coat is bonded to the backing sheet in a transfer-lamination process such as that described  
in the above-referenced U.S. Patent 5,707,697 to Spain et al. The size coat comprises any  
synthetic resinous material which is heat activated during the transfer-lamination step to bond  
20 the paint coat to the backing sheet. A preferred dry film thickness of the size coat is from about  
0.1 to about 1.0 mil. The size coat is preferably applied as a thermoplastic paint coat and dried  
in the same multi-stage drying step used in drying the clear coat and color coat. For a  
PVDF-acrylic based paint system, an acrylic resin based size coat is preferred for suitable  
bonding of the paint coat to the backing sheet. In one embodiment, in which the paint coat is  
25 adhered to a backing sheet made of acrylonitrile-butadiene-styrene (ABS) this size coat can  
comprise a polymethyl-methacrylate resin dissolved in a suitable solvent and dried. In another  
embodiment, in which the backing sheet is a thermoplastic polyolefin, or is made from an  
olefinic material such as polypropylene, the size coat can comprise a composite of an acrylic  
resin layer for bonding to the color coat and a suitable chlorinated polyolefin bonding layer for  
30 bonding to the olefin-based backing sheet.

FIG. 2 illustrates a coextrusion process for making the backing sheet 16 and its adhesive  
layer 18. In one embodiment the coextrusion is made from starting materials comprising an  
acrylic resin A and an ABS resin B. Both resin materials are fed to separate driers 20 for  
removing excess moisture before extruding. Dried resin pellets of each material are fed from the  
35 drier into hoppers 22 via vacuum tubes 24. From the hoppers the pellets are gravity fed to  
separate extruders 26. The pellets are fed into the feed section of each extruder barrel. The  
resins in each extruder are heated to a molten state and fed through their respective barrel  
sections to a single combining block 28 and then into the die 30 of an extruder 32. The molten



1 coextruded sheet exits the die and runs through a three-roll calendering (polishing) stack  
comprising an upper roller 34, an intermediate roller 36, and a bottom roller 38. The calendering  
operation polishes both sides of the coextruded sheet. The sheet then passes downstream away  
from the extruder and is cooled by passing over chill rolls 40 and is finally wound on an exit roll  
5 42. In one embodiment, the final coextruded sheet comprises from about 0.8 to about 1.5 mils  
acrylic lacquer adhesive layer and a 28.5 mil ABS backing sheet layer. Other embodiments also  
are useful in practicing the invention as described in examples below.

FIG. 3 shows a transfer-lamination process for applying the dry paint transfer film to the  
backing sheet. In the process illustrated in FIG. 3 the backing sheet can either comprise a  
10 separate backing sheet with an adhesive size coat as described in U.S. Patent 5,707,697 to Spain  
et al., or it can comprise the coextruded sheet described with reference to FIG. 2. Referring to  
FIG. 3 the laminating step includes the paint coated carrier stored on a top unwind roll 44 and  
a flexible adhesive coated backing sheet stored on a bottom unwind roll 46. The carrier and  
backing sheet pass between a heated laminating drum 47 and a rubber backup roll 48. The  
15 laminating drum is preferably made of steel and operated at a temperature of about 400° to  
425°F. It is pressed into contact with the overlapping sheets to heat them to a temperature  
sufficient to activate the adhesive layer and press the two sheets into contact with each other to  
bond the paint coat to the backing sheet. The rubber backup roll 48 is pressed into contact with  
the laminating roll preferably at a pressure of about 300 pounds per lineal inch. The polyester  
20 carrier sheet on which the paint film is cast is stripped away from the paint film and passed to  
a take-up roll 49. A thin protective film such as polyvinyl acetate is unwound from a storage roll  
50 and laminated to the clear coat side of the paint film by laminating rolls 51. The sheets travel  
around the drums 60, 62 and 64 at a slow speed during laminating to ensure that the resulting  
lamine 52 is heated to a temperature approaching the temperature of the laminating drum. This  
25 softens the backing sheet material somewhat as well as activating the adhesive layer to ensure  
a complete bond between the paint coat and the backing sheet. The polyester carrier sheet of the  
paint coated film has a heat resistance well above laminating temperature so the carrier resists  
elongation during the laminating step. Following the transfer-lamination or bonding step, the  
flexible paint coated laminate 52 is then passed around one or more chill rollers (not shown) for  
30 cooling the laminate to room temperature. Prior to passing around the chill rolls the film is  
laminated with the protective outer film 50 while the top coat is warm. The finished laminate  
52 then passes onto a laminate rewind drum 54.

The coextrusion process of FIG. 2 simplifies the production process when compared with  
a process for producing a preformed backing sheet and laminating it to a paint film to which the  
35 size coat has been solvent cast. By coextruding the backing sheet and adhesive layer, the step  
of separately coating the size coat to the dry paint film by a reverse roll coater is eliminated.

Referring to FIG. 4, the preformed paint film laminate 52 is next laminated to the top of  
a thick polymeric substrate sheet preferably when the substrate sheet is extruded. A thick

1 substrate sheet 56 is initially extruded from the die of an extruder 58. The extruded sheet then  
passes through a three-roll calendaring stack comprising an upper roll 60, an intermediate roll  
62 and a bottom roll 64. The extruded sheet first passes between the upper and intermediate rolls  
5 which are operated at temperatures for immediately cooling the sheet to stabilize it. The sheet  
is also polished on both sides by the rolls. The extruded sheet then wraps around the  
intermediate roll 62 and passes between the nip of the rolls 62 and 64. At the same time, the  
paint film laminate 52 is unwound from roll 54 and passes into the nip of the same rolls 62 and  
64. This applies heat and pressure to fuse the backing sheet side of the laminate 52 to one side  
10 of the extruded thick sheet 56. This extrusion lamination step produces a composite thick sheet  
laminate 66 with the paint film laminate bonded as an integral unit to the extruded thick sheet  
substrate. Preferably, the bottom roll 64 of the stack is operated at a lower temperature than the  
other two rolls for providing further temperature reductions in the lamination step. The preferred  
approach is to pass the paint film laminate 52 through the nip on the side contacted by the bottom  
roll 64 of the stack so that its lower roll temperature is applied directly to the carrier sheet side  
15 of the paint film laminate when joining the laminate to the extruded sheet 56.

FIG. 5 illustrates an alternative extrusion-lamination process similar to FIG. 4, but with  
a modification that accommodates lamination of paint film-backing sheet laminates to thinner  
extruded substrate sheets. In FIG. 5 the paint film-backing sheet laminate 52 is bonded to the  
extruded sheet at a higher point on the intermediate roll 62. The laminate 52 in this instance is  
20 applied at the nip of the intermediate roll 62 and a separate laminating roll 67. The purpose is  
to raise the level of the nip closer to the center of the roll 62 for thinner extruded substrates (say  
in the 40 mil range) and to gradually lower the nip to the point shown in FIG. 4 for thicker  
extruded substrate sheets (say in the 200 to 250 mil range). The adjustment of the nip location  
maintains desirable paint film temperatures so they are not adversely affected as residual heat  
25 in the substrate increases.

The thick substrate sheet is extruded at a thickness that coincides with the desired  
thickness of the finished part. According to the present invention, an objective is to avoid a  
subsequent injection molding step in forming the substrate component of the finished part. The  
extruded substrate sheet component provides the necessary rigidity or structural integrity of the  
30 finished part, and yet the substrate sheet must be sufficiently thermoformable to be shaped by  
thermoforming into the desired contour of the finished part. In one form of the invention, the  
extruded substrate sheet has a minimum thickness of at least about two to about three times the  
thickness of the backing sheet. In one embodiment, the backing sheet is about 10 to 12 mils  
thick and the extruded substrate sheet is about 48-50 mils thick. In another embodiment, the  
35 backing sheet is about 18 to 20 mils thick and the extruded substrate sheet is about 0.20 to  
0.25 inch thick. Insofar as relative dimensions are concerned, the backing sheet preferably has  
a thickness in the range of about 10 to about 30 mils, and the extruded thick substrate sheet has  
a thickness in the range from about 40 mils to about 0.25 inch.

1           The substrate sheet 56 is preferably made from a material comprising essentially the same  
polymeric composition or at least a polymeric composition compatible with the polymeric  
material contained in the backing sheet, in the sense that the two materials may be compatibly  
fused together under heat as an integral structural unit. In one form of the invention, the thick  
5       substrate sheet material is extruded as illustrated in FIG. 4, and the substrate material is sufficient  
to fuse to the backing sheet using the heat of extrusion to heat bond the two sheets together as  
an integral unit by melt adhesion techniques. The preferred materials from which the thick  
substrate sheet is made are ABS, for bonding to an ABS backing sheet, or TPO including  
polypropylene or polyethylene when bonding the thick sheet to similar compatible materials  
10       contained in the backing sheet. The paint film on the surface of the finished laminate 66 has a  
defect-free surface, maintaining the desired optical properties of an automotive quality paint  
finish. Any defects in the substrate material, such as filler particles or regrind material, are  
absorbed by the intervening backing sheet to provide the defect-free paint coat.

During extrusion-lamination the molten material extruded at the die opening of the  
15       extruder typically has a temperature of about 400°F to 450°F, depending upon the polymeric  
extruded material. The temperature at which lamination takes place is substantially lower owing  
to the temperature reduction produced by the calendaring rolls next to the extruder die exit  
opening. In one embodiment, the upper roll 60 is operated at a temperature in the range of about  
200°F to about 216°F, the intermediate roll 62 is operated at a temperature in the range of about  
20       175°F to about 210°F, and the bottom roll 64 is operated at a temperature in the range of about  
150°F to about 205°F. This lowers lamination temperature at the nip of the intermediate and  
lower calendaring rolls to about 380°F to about 420°F. At these temperature levels the paint  
film laminate can be successfully bonded to the extruded thick substrate sheet while the  
necessary heat levels do not adversely cause haze or fogging of the paint film. These roll  
25       temperatures are cited as examples only and can be adjusted for controlling heat bonding and  
absorbed heat levels at the paint film to ensure optical clarity of the finished film, depending  
upon the materials used. It should be noted that in the process of FIGS. 4 and 5, the protective  
sheet 50 which was applied in the processing step of FIG. 3 remains intact as a protective cover  
for the paint film during the extrusion-lamination process and the subsequent forming step. The  
30       protective sheet also is left in place after the forming step to protect the outer clear coat surface  
from abrasion.

Referring to FIG. 6, the thick sheet laminate 66 is thermoformed into a desired three  
dimensional shape of the finished part. The initially flat laminate can be formed into a highly  
contoured three dimensional shape for use as a finished exterior automotive car body panel or  
member. FIG. 7 schematically shows a three dimensionally shaped thick sheet laminate 68  
35       which has been thermoformed to a finished three dimensional shape following thermoforming.  
In one embodiment, the thick sheet laminate 66 can be thermoformed and trimmed to produce  
a finished automotive part, such as a facia or a body side molding trim part, each of which are

1 ready to be put on a vehicle. The process avoids a subsequent molding step for forming a  
molded substrate or structural component of the finished part. The thermoforming step can be  
carried out by various types of thermoforming equipment. During thermoforming, the thick  
sheet laminate is preheated to a thermoforming temperature in an oven, followed by vacuum  
5 forming the sheet into a desired three dimensional shape. The thermoforming temperature is in  
a range which allows softening and thermoplastic elongation of the paint film and its supporting  
sheet to form the finished part. The actual sheet temperature to which the paint film is subjected  
(not oven temperature) is at a level that prevents deglossing of the paint film during  
thermoforming. In one embodiment, sheet temperatures during thermoforming range from about  
10 310°F to about 360°F at the paint film surface of the sheet. The core temperature of the thick  
substrate sheet also is raised to a temperature substantially within the same temperature range  
so that heat transmitted to the paint film surface from the substrate does not adversely affect  
optical properties of the paint film. When the thick sheet laminate is preheated in the  
thermoformer oven to raise its core temperature to a desired thermoforming temperature, it is  
15 desirable to apply proportionately more heat to the back side of the laminate than to the front side  
of the film. By applying approximately zero to 30% of the heat to the front side and  
approximately 70% to 100% of the heat to the back side, the back side of the laminate ends up  
about 20°F to 30°F hotter than the front side. This produces about 20% higher DOI and about  
10% higher gloss than a more evenly distributed application of heat. The desired oven  
20 temperature of the thermoformer is about 450°F to 650°F, and this temperature can vary  
depending upon the thickness of the substrate sheet, and the desired cycle times. For a 60 mil  
thick sheet for example, cycle time is about 1.5 to 2 minutes for heating the laminate to its  
forming temperature. Sheet temperatures in the 340°F to 360°F range produce the best  
combination of DOI and gloss, in one trial.

25 FIG. 8 illustrates a post-processing step in which fasteners or reinforcing members can  
be applied to the finished laminate 68 for use in converting the finished part into a structural  
panel. The illustrated process is an example of a twin sheet forming process in which an  
attachment mechanism 70 is embedded in a final laminated sheet 72. The process includes  
starting with the thick sheet laminate 68 at a storage roll 74 and a separate thick polymeric  
30 substrate sheet 76 on a storage roll 78. The two thick sheets pass around separate rolls 80 and  
are fed to a thermoformer as separated sheets. A preheater 82 located between the sheets  
preheats both sides of the sheets, along with main heaters 84. The reinforcement mechanism or  
fastener 70 is inserted into the void space prior to the forming station where forming tools 86  
apply heat and pressure to the two sheets to bond them together as an integral structural unit 88  
35 with the attachment device or reinforcement embedded in the final part. The two joined sheets  
also can be shaped to a contour in the former. This can produce structural parts where the twin  
substrate sheets (the laminate 68 and the sheet 76) can each have a thickness in the range of 200  
to 250 mils. for example, and be bonded together to form the thick structural part 88.

1 As an alternative, the finished part 68 can have fastener or reinforcement parts attached to it by conventional welding, spin welding or sonic bonding techniques.

Example 1

5 Weatherable thermoplastically formable paint films for use in this invention can be made from many suitable polymeric materials and formulations. One such paint system useful in practicing this invention comprises a base coat/clear coat paint system in which each paint film layer comprises an alloy of PVDF and acrylic resins. Such exterior automotive paint films are available from Avery Dennison Corporation under the trademark AVLOY®. A clear coat  
10 formulation useful in practicing this invention comprises about 60% PVDF and about 40% acrylic resin, by weight, based on the total resin solids contained in the dry paint film. A typical clear coat formulation, based on parts by weight, is as follows:

	<u>Ingredients</u>	<u>Parts</u>
15	PVDF (KYNAR 500 plus homopolymer - Elf Atochem)	20.0
	Polyethyl methacrylate (ELVACITE 2042-ICI)	12.0
	Dispersing agent (Solsperse 17000)	0.06
	UV absorber (Tinuvin 900)	0.64
20	Cyclohexanone	19.52
	Exxate® 700 - Exxon Chemicals	21.53
	Butylactone (BLO)	26.25

25 A color coat formulation useful in practicing this invention also comprises about 60% PVDF and about 40% acrylic resin, by weight of the total resin solids contained in the dry film. In this instance a portion of the acrylic resin solids content is provided by the acrylic resin vehicle for the pigment dispersion. A typical color coat formulation for a jet black automotive paint film is as follows:

30

35

1		<b><u>Ingredients</u></b>	<b><u>Parts</u></b>
		PVDF (KYNAR 500 plus - Elf Atochem)	16.90
		Polyethyl methacrylate (ELVACITE 2042)	10.14
5		Dispersing agent (Solsperse 17000)	0.05
		UV absorber (Tinuvin 900)	0.54
		Black pigment dispersion	14.72
		Blue pigment dispersion	0.78
10		BLO	22.19
		Exxate® 700	18.19
		Cyclohexanone	16.49

The pigment dispersions contained in the color coat can vary, depending upon the choice of color. The following pigment dispersions are used in the preceding color coat formulation.

The black dispersion designated as 474-39350 pigment dispersion from Gibraltar Chemical comprises:

		<b><u>Ingredients</u></b>	<b><u>Parts</u></b>
		Pigment - (FW 206 DeGussa)	7.0
20		Acrylic resin - (B735 - Zenica)	29.7
		Exxate 600 - (Exxon Chemicals)	31.65
		BLO	31.65

The blue dispersion designated as 474-34550 pigment dispersion from Gibraltar comprises:

		<b><u>Ingredients</u></b>	<b><u>Parts</u></b>
		Pigment (Palomar Blue - Bayer)	9.10
		Acrylic resin - B735	22.30
30		Exxate 600	34.3
		BLO	34.3

Various other pigmented color coats can be used without departing from the scope of the invention. In addition to basic pigmented color coats and metallic automotive paints, the color coat also can include print patterns such as Silver Brush sold under the designation AVLOY® by Avery Dennison Corporation. This color coat consists of a base coat comprising a dispersion of metal flake sold under the designation METALURE® by Avery Dennison, together with suitable print coats between the base coat and clear coat, to provide the finished pattern.

1           The clear coat/color coat paint film may be cap sheet laminated either to a thick ABS  
substrate sheet or to a thick TPO substrate sheet. In the ABS embodiment, an acrylic adhesive  
layer approximately 0.8 to 1.5 mils in thickness is coextruded with an ABS backing sheet  
approximately eleven mils in thickness. The acrylic adhesive is made from acrylic resin  
5       materials such as AutoHaas DR 101 or Cyro HS116. The ABS backing sheet is extruded from  
a premium grade material having a low gel count, such as LSA from General Electric. In one  
embodiment the extruded thick substrate sheet was extruded at a thickness of about 49 mils and  
was made from a lower grade general purpose ABS composition having up to 30% regrind  
materials, such as LS 1000 from G.E. In a similar embodiment an 18 mil thick high grade ABS  
10       sheet was cap sheet laminated to a 40 mil thick extruded ABS blended with regrind materials.

          In an embodiment comprising a TPO substrate, the adhesive layer is cast as a dual-layer  
size coat, first with an acrylic size coat for bonding to the color coat side of the paint film, and  
second, with a chlorinated polyolefin (CPO) size coat cast on the acrylic size coat, for bonding  
to a TPO backing sheet. The acrylic size coat can comprise ELVACITE 2042 PEMA resin  
15       solvent cast from suitable solvents and dried to a film thickness of about  $12\text{gm/m}^2$ . The CPO  
size coat can comprise DuPont 826 or Hardlyn CP13 resins, solvent cast from suitable solvents  
and dried to a film thickness of about  $12\text{gm/m}^2$ . In one embodiment, the TPO backing sheet can  
be a preformed 20 mil thick premium grade TPO such as E 1501 or E 900 from Solvay or R370  
from Royalite. The extruded thick TPO substrate sheet can have a thickness from about 0.20 to  
20       0.25 inch and can be made from lower grade materials from the same suppliers.

### Example 2

          The objective of this trial was to make a coextruded sheet comprising an acrylic resin  
adhesive layer and an ABS resin backing sheet. Both the acrylic resin and ABS resin starting  
25       materials require drying of excess moisture before extruding. This is accomplished by drying  
the resin in a desiccant dryer for at least 2 hours at 150°F for the acrylic resin and 170°F for the  
ABS. During extrusion additional resin is added to the dryers as resin is pumped to the extruder  
via vacuum lines. While running, the dryers are set at 200°F to dry the resin constantly input  
to the dryer. The resin should have a final moisture content below 0.08% moisture content to  
30       prevent problems with extrusion. The desired moisture content level for extrusion is between  
about 0.02% to 0.04%. The dried resin pellets of each material are fed into the hoppers on the  
top of each extruder via vacuum tubes. From the hoppers the pellets are gravity fed into the feed  
section of the extruder barrel. They are screen fed through the barrel and heated to a molten  
state. The resins in the two extruders are fed through their respective barrel sections to a single  
35       combining block and then into the die of the extruder. The molten sheet exits the die and runs  
through a 3-roll calendaring stack which polishes both sides of the sheet. As the sheet travels  
down the line it is cooled by passing over chilled steel rolls and finally is wound up into a roll.  
In one embodiment the final roll comprised about 0.8 to about 1.5 mil acrylic lacquer and a 28.5

1 mil ABS layer for a total sheet thickness of 30 mils. Final melt temperatures of the molten resin were as follows:

	<u>Barrel zone</u>	<u>Die Zone</u>
5	1 - 430°F	1 - 480°F
	2 - 410	2 - 470
	3 - 420	3 - 430
	4 - 409	4 - 450
	5 - 404	5 - 460
10	<u>Adapter</u>	<u>Flange</u>
	A1 - 400°F	<u>mixer slide</u>
	A2 - 400	480°F 450°F
	<b>Co-extrusion block:</b>	400°F

15 Die temperature is 440°F for all zones, and melt temperature is 408°F. Line speed is 39.8 ft/min. In the 3-roll calendaring stack the start temperatures of the top, middle and bottom rolls were 170°F, 150°F and 145°F, respectively.

### 20 Example 3

Extrusion cap sheet lamination trials were conducted according to principles of this invention. Suitable cap sheet lamination equipment is available from Spartech, Portage, WI. In one trial a 20 mil thick dry paint film-backing sheet laminate was cap sheet laminated to a 0.22 inch thick extrusion of 100% re-pelletized E900 TPO. Avloy® dry paint transfer films available from Avery Dennison Corporation, such as AL310036 G3, AL310043 G3 and AL310056 G3, were laminated to the 20 mil thick backing sheet of TPO material and then cap sheet laminated to the 0.22 inch extruded TPO sheet, using the heat of extrusion to laminate the backing sheet side of the preformed paint film laminate to the thick extruded substrate. In this embodiment the upper, intermediate and lower roll temperatures at the extruder die exit were 210°F, 210°F and 150°F, respectively. In another trial a 22 mil thick dry paint laminate was laminated to a 0.230 inch TPO sheet. The upper roller at the extruder die exit in this instance was at 216° F. The process produced a 0.25 inch thick composite laminate ready for thermoforming to a finished automotive body panel.

35 Thus, the thin thermoformable backing sheet can be made from a high quality polymeric material free of gels or other defects, and the backing sheet will mask any gels or other defects in the extruded thick sheet to prevent them from being transmitted to the paint film side of the finished part during thermoforming. As a result, a lower grade of polymeric materials can be used for the extruded thick substrate sheet. By using a lower grade substrate material as a major



1      portion of the final construction. the process provides significant cost savings. By  
thermoforming the part out of a material thick enough to be directly put onto the car, the need  
for injection molding the substrate component, including costly injection molding equipment and  
special tooling, is avoided, further reducing production costs.

5

10

15

20

25

30

35

## 1 CLAIMS

1. A process for making an exterior automotive quality body panel member from a preformed dry paint transfer laminate comprising an exterior automotive quality paint film applied to a relatively thin semi-rigid thermoformable polymeric backing sheet, comprising the steps of extruding a relatively thick sheet comprising a thermoformable polymeric material;

forming a paint-coated thick sheet laminate by laminating the backing sheet side of the preformed dry paint laminate to the extruded sheet, using the heat of extrusion to heat bond the backing sheet and extruded sheet together to form an integral substrate sheet which is thermoformable to a three-dimensional shape with the dry paint film bonded to its surface, the backing sheet and extruded sheet comprising compatible polymer materials to promote the bond between them, the extruded sheet having a thickness at least twice the thickness of the backing sheet;

applying heat to the resulting thick sheet laminate to raise the substrate sheet to a forming temperature; and

forming the laminate to a three-dimensional shape to produce a finished exterior automotive quality body panel or member.

2. The process according to claim 1 in which the polymeric material of the backing sheet has a lower gel count than the thicker extruded sheet material.

3. The process according to claim 2 in which the polymeric material of the extruded substrate sheet has a substantially higher filler content than the backing sheet material.

4. The process according to claim 1 in which the extruded sheet has a thickness at least three times the thickness of the backing sheet.

5. The process according to claim 1 including applying heat to the thick sheet laminate by a temperature gradient in which the amount of heat applied to the substrate side of the laminate is greater than the amount of heat applied to the paint film side in raising the temperature of the laminate to its forming temperature.

6. The process according to claim 1 in which the dry paint transfer film comprises an exterior automotive base coat/clear coat paint film and in which the distinctness-of-image of the finished thermoformed panel is greater than about 60.

7. The process according to claim 1 including coextruding the backing sheet and an adhesive layer on the backing sheet for bonding to the dry paint transfer film.

1  
8. The process according to claim 7 in which the coextrusion step is followed by dry paint transfer lamination of the dry paint film to the adhesive side of the coextrusion.

5 9. A process for making an extruded exterior automotive body panel or member comprising the steps of providing a preformed dry paint transfer laminate comprising an exterior automotive quality paint film applied to a relatively thin semi-rigid thermoformable polymeric backing sheet having a thickness in the range from about 10 mils to about 30 mils;

10 extruding a relatively thick sheet comprising a thermoformable polymeric material;  
forming a paint coated thick sheet laminate by laminating the backing sheet side of the preformed dry paint laminate to the extruded sheet using the heat of extrusion to heat bond the backing sheet and extruded sheet together to form an integral substrate sheet which is thermoformable to a three-dimensional shape with the dry paint film bonded to its surface, the  
15 backing sheet and extruded sheet comprising compatible polymeric materials to promote the bond between them, the extruded sheet having a thickness of at least about 40 mils;

applying heat to the resulting thick sheet laminate to raise the substrate sheet to a forming temperature; and

20 forming the laminate to a three-dimensional shape to produce a finished exterior automotive quality body panel or member.

10. The process according to claim 9 in which the polymeric material of the backing sheet has a lower gel count than the thicker extruded sheet material.

25 11. The process according to claim 10 in which the polymeric material of the extruded substrate sheet has a substantially higher filler content than the backing sheet material.

12. The process according to claim 9 in which the extruded sheet has a thickness at least three times the thickness of the backing sheet.

30 13. The process according to claim 9 including applying heat to the thick sheet laminate by a temperature gradient in which the amount of heat applied to the substrate side of the laminate is greater than the amount of heat applied to the paint film side in raising the temperature of the laminate to its forming temperature.

35 14. The process according to claim 9 in which the dry paint transfer film comprises an exterior automotive base coat/clear coat paint film and in which the distinctness-of-image of the finished thermoformed panel is greater than about 60.

1  
15. The process according to claim 9 including coextruding the backing sheet and a adhesive layer on the backing sheet for bonding to the dry paint transfer film.

5 16. An exterior automotive quality body panel or member comprising a dry paint transfer film for providing a layer of color to the exterior of the finished panel or member; a relatively thin semi-rigid polymeric backing sheet adhered to the dry paint transfer film; a relatively thick supporting sheet of a thermoformable polymeric material laminated to the backing sheet, heat bonded thereto to form an integral substrate sheet which is thermoformed to a three-dimensional shape with the dry paint transfer film bonded to its outer surface;

10 the backing sheet and extruded sheet comprising compatible polymeric materials to promote the bond between them, the polymeric material of the backing sheet having a lower gel count than the thicker exterior substrate material, the polymeric material of the substrate sheet having a substantially higher filler content than the backing sheet material, the relatively thicker supporting sheet component of the substrate having a thickness at least twice the thickness of the backing sheet;

15 the thermoformed three-dimensionally contoured body panel or member having an exterior outer surface of exterior automotive quality in the absence of appreciable haze caused by thermoforming to its finished shape.

20 17. The process according to claim 7 in which the dry paint transfer film comprises a base coat/clear coat film having a distinctness-of-image greater than about 60.

25 18. The product according to claim 17 in which the backing sheet has a thickness in the range of about 10 mils to about 30 mils and the relatively thicker supporting sheet has a thickness of at least about 40 mils.

30 19. The product according to claim 17 in which the supporting sheet is bonded to the backing sheet by the heat of extrusion of the supporting sheet and the laminating pressure in joining the two sheets together as a composite integral sheet.

FIG. 1

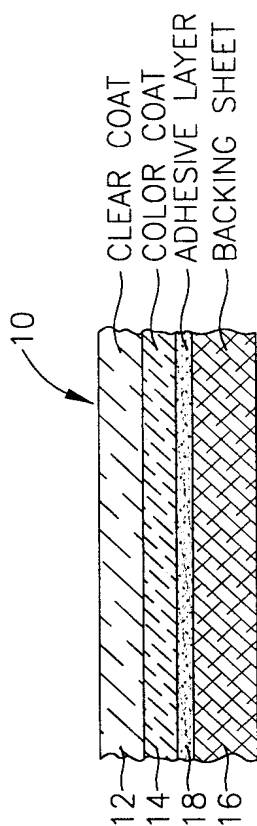
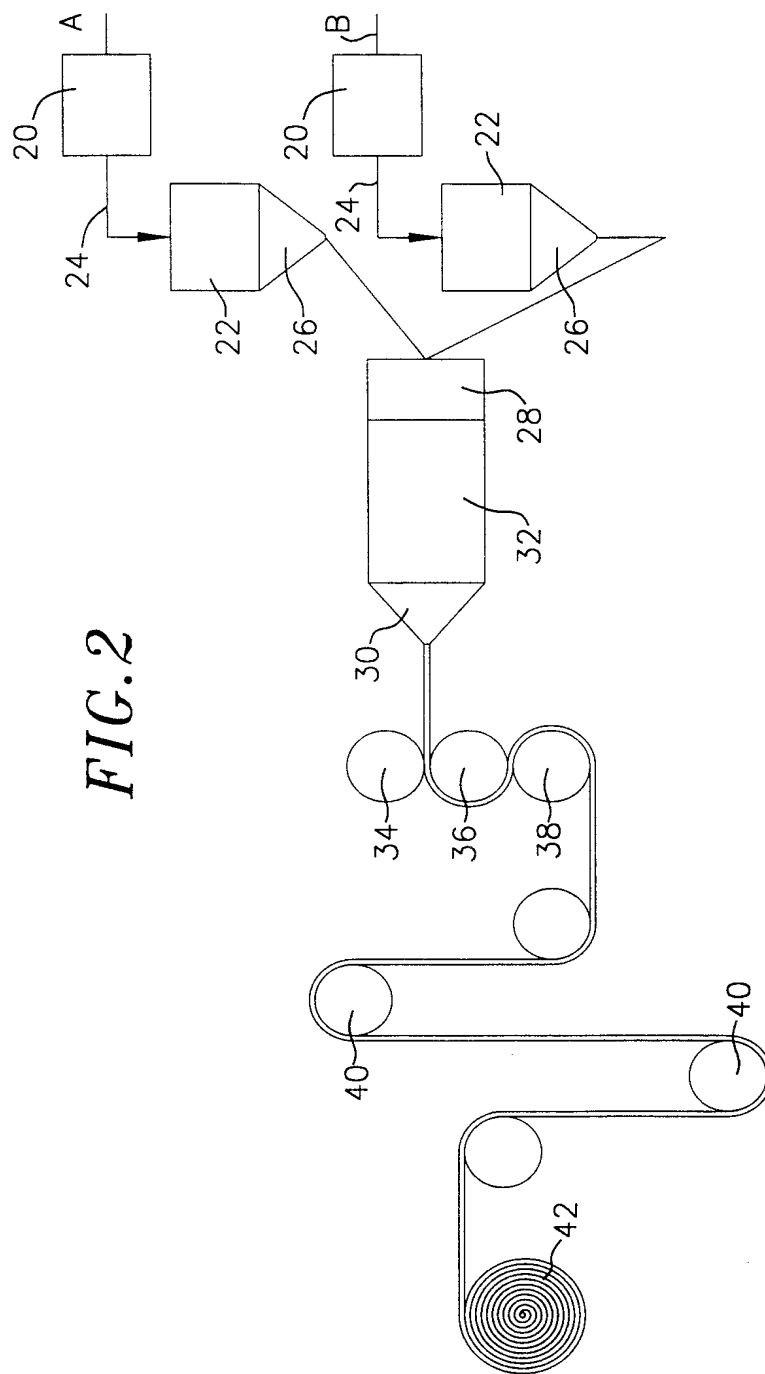


FIG. 2



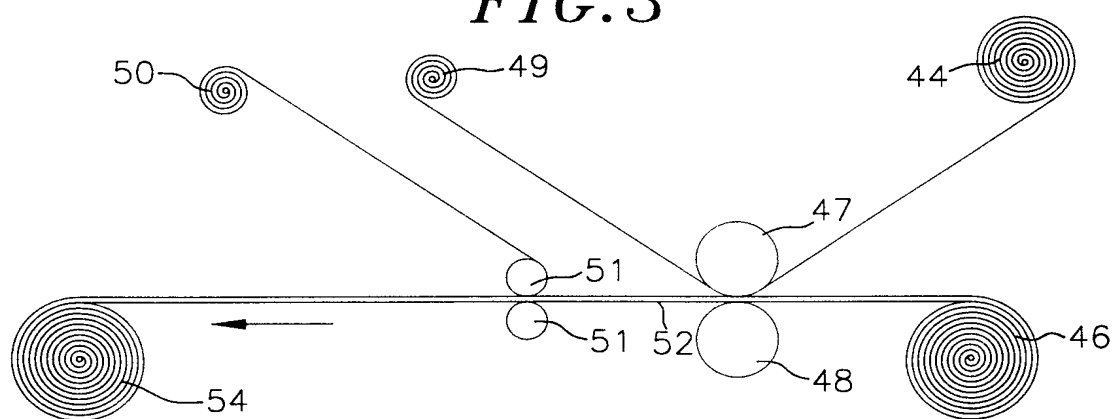
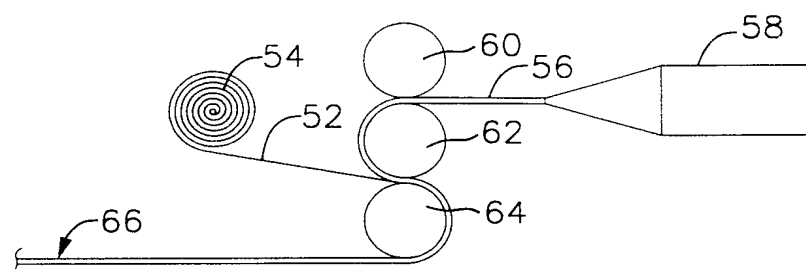
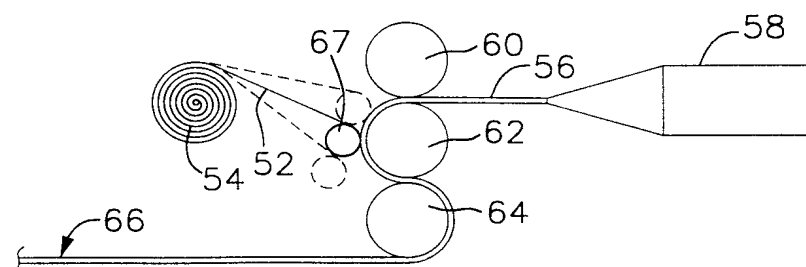
*FIG. 3**FIG. 4**FIG. 5*

FIG. 6

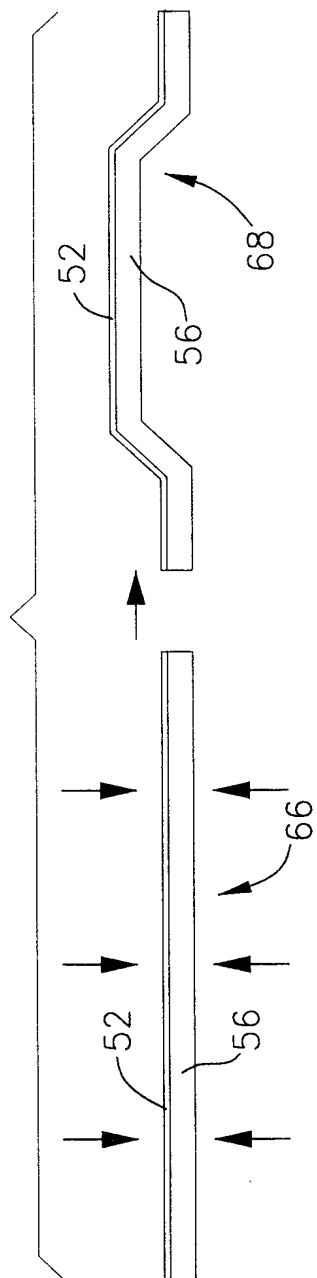


FIG. 7

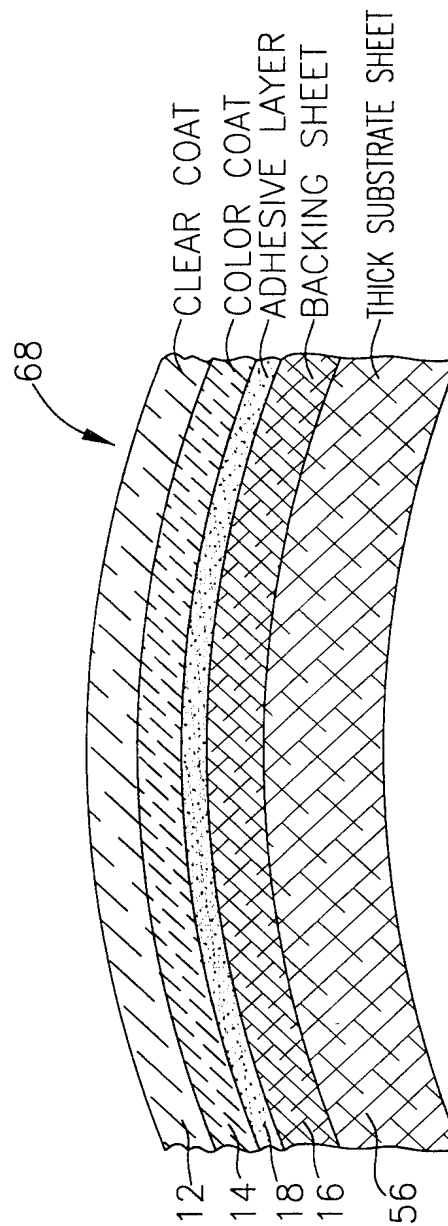
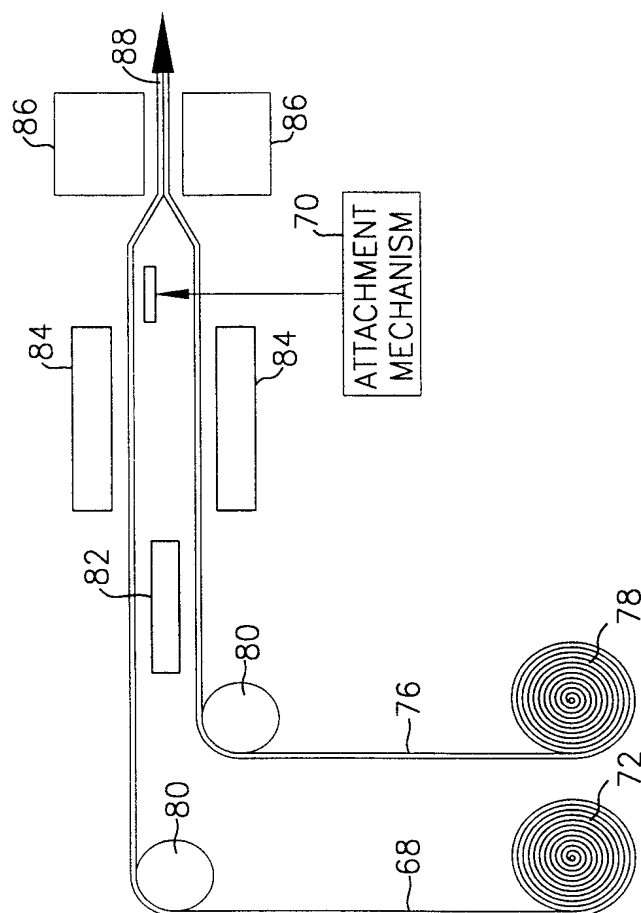


FIG. 8





# INTERNATIONAL SEARCH REPORT

International Application No  
PC1/US 99/12668

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B32B31/30 B32B27/20 B32B27/30 B29C51/14 //B29K27:12,  
B29K33:04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B B29C B60R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 40519 A (AVERY DENNISON CORPORATION) 19 December 1996 (1996-12-19)  page 37, paragraph 2; figures 12,18,20; example 8 ---	1,2,4,7, 9,10,12, 15
A	WO 89 06598 A (DU PONT) 27 July 1989 (1989-07-27) page 16, line 31 -page 17, line 8; claims 1,20; figures 1,,1A ---	2,10,16
A	GB 1 225 438 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 17 March 1971 (1971-03-17) page 1, line 49 - line 82 page 2, line 41 - line 125; claims 1-9 --- -/--	4,9,12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"&" document member of the same patent family

Date of the actual completion of the international search

5 October 1999

Date of mailing of the international search report

14/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Van Nieuwenhuize, 0

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/12668

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 42 28 194 A (H P CHEMIE PELZER RES & DEV) 3 March 1994 (1994-03-03) column 6, line 30 -column 7, line 38; claims 1,11,15 ---	4,9,12
A	US 4 515 649 A (NUSSBAUM JOEL H) 7 May 1985 (1985-05-07) column 7, line 4 - line 7; claims 1,3; figure 6 ---	1,9
A	US 5 342 666 A (KEITH BRIAN M ET AL) 30 August 1994 (1994-08-30) claim 1; figure 5 ---	4,9,12, 16
A	WO 90 06857 A (EASTMAN KODAK CO) 28 June 1990 (1990-06-28) claims 1,3 ---	1,9,16
A	DE 29 38 462 A (UGINE KUHLMANN COURBEVOIE PROD) 27 March 1980 (1980-03-27) claim 10 ---	1
A	DATABASE WPI Week 8948 Derwent Publications Ltd., London, GB; AN 1989-354225 XP002117598 & JP 01 267018 A (DAINIPPON PRINTING), 24 October 1989 (1989-10-24) abstract -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/12668

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9640519 A	19-12-1996	AU 6330996 A CA 2223902 A EP 0831998 A	30-12-1996 19-12-1996 01-04-1998
WO 8906598 A	27-07-1989	US 4902557 A AT 139183 T CA 1337858 A DE 68926669 D DE 68926669 T EP 0398928 A JP 3502432 T	20-02-1990 15-06-1996 02-01-1996 18-07-1996 02-01-1997 28-11-1990 06-06-1991
GB 1225438 A	17-03-1971	DE 1946820 A NL 6914081 A	06-05-1970 19-03-1970
DE 4228194 A	03-03-1994	AT 149918 T BR 9306960 A CZ 9500496 A DE 59305798 D WO 9404358 A EP 0658141 A ES 2101338 T JP 8500539 T	15-03-1997 12-01-1999 13-12-1995 17-04-1997 03-03-1994 21-06-1995 01-07-1997 23-01-1996
US 4515649 A	07-05-1985	US 4349592 A AR 226079 A AU 536276 B AU 6305180 A CA 1151706 A DE 3039082 A ES 495805 A FR 2486873 A GB 2080193 A, B IT 1133178 B JP 1458175 C JP 57032939 A JP 63007132 B	14-09-1982 31-05-1982 03-05-1984 21-01-1982 09-08-1983 11-02-1982 16-10-1981 22-01-1982 03-02-1982 09-07-1986 09-09-1988 22-02-1982 15-02-1988
US 5342666 A	30-08-1994	US 5514427 A US 5536539 A US RE35894 E US RE35970 E AT 71574 T CA 1292603 A DE 3776076 D EP 0266107 A JP 1731362 C JP 4020782 B JP 63120640 A KR 9404023 B	07-05-1996 16-07-1996 08-09-1998 24-11-1998 15-02-1992 03-12-1991 27-02-1992 04-05-1988 29-01-1993 06-04-1992 25-05-1988 11-05-1994
WO 9006857 A	28-06-1990	US 5114789 A CA 2005937 A DE 68910987 D DE 68910987 T EP 0449982 A JP 4502287 T US 5286528 A	19-05-1992 20-06-1990 05-01-1994 23-06-1994 09-10-1991 23-04-1992 15-02-1994

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/12668

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 2938462 A	27-03-1980	FR 2436676 A	18-04-1980
		FR 2457180 A	19-12-1980
		AR 218396 A	30-05-1980
		AT 379107 B	25-11-1985
		AT 628479 A	15-04-1985
		AU 527970 B	31-03-1983
		AU 5116079 A	03-04-1980
		BE 878845 A	18-03-1980
		BG 49714 A	15-01-1992
		BR 7906102 A	03-06-1980
		CA 1130525 A	31-08-1982
		DD 146023 A	21-01-1981
		DK 116180 A	19-09-1981
		ES 484407 A	16-12-1980
		FI 792968 A,B,	26-03-1980
		GB 2031795 A,B	30-04-1980
		GR 65674 A	16-10-1980
		IE 48693 B	17-04-1985
		IN 153223 A	16-06-1984
		IT 1119928 B	19-03-1986
		JP 1716530 C	14-12-1992
		JP 3013059 B	21-02-1991
		JP 55044898 A	29-03-1980
		KR 8300832 A	20-04-1983
		LU 81717 A	17-04-1981
		NL 7907106 A	27-03-1980
		PT 70215 A	01-10-1979
		RO 78589 A	24-03-1982
		SE 445193 B	09-06-1986
		SE 7907864 A	26-03-1980
		SI 7912323 A	31-08-1997
		SU 1071216 A	30-01-1984
		US 4317860 A	02-03-1982
		US 4415519 A	15-11-1983
		YU 232379 A	21-01-1983
		ZA 7905036 A	24-09-1980
		CS 219907 B	25-03-1983
JP 1267018 A	24-10-1989	JP 2600273 B	16-04-1997